Efficient visible light-induced photoelectrochemical oxidation of water was achieved using a tungsten(IV) oxide (WO₃) film composed of perpendicularly oriented plate-like crystallites, a flake-wall film, prepared on a transparent conductive substrate by controlling anisotropic crystal growth of tungsten oxide hydrate (WO₃•H₂O) followed by calcination.

Water splitting using solar light is a key technology for the establishment of a low-carbon society. Because of the positive Gibbs energy change in the water splitting, a direct one-step reaction may not proceed even though compensating energy is injected from outside the system, but it can be achieved by dividing into two parts: reduction of water to hydrogen and oxidation of water. Fujishima and Honda reported, for the first time, that photoradiated titania and platinum electrodes could be used for the oxidation and reduction parts, respectively. Although such a "photoelectrochemical" cell requires additional external energy as electrical or chemical bias to compensate the potential drop due to resistance of a circuit as well as overpotentials for the redox (electron transfer) reactions, the anode and cathode can be designed and their performance can be optimized separately and individually, which is the most significant merit of photoelectrochemical systems compared with particulate photocatalytic systems. Photoelectrochemical oxidation of water to evolve molecular oxygen is induced on an n-type semiconductor electrode by valence band holes generated by band-gap excitation. Significant incident photon-to-current conversion efficiencies (IPCEs) for oxidation of water have been reported on WO₃ films, which are responsive to the blue part of visible light owing to the band gap of ca. 2.6 eV. Nanocrystalline WO₃ films prepared by sol-gel techniques possessed porous network structures consisting of well-crystallized nanoparticles exhibiting a large surface area for semiconductor/liquid junctions. Since porous electrodes require a thickness of several micrometers to maximize light absorption, the increase in thickness would increase grain boundaries, at which free electrons are scattered and recombination of photogenerated electron-hole pairs occurs, resulting in retardation of electron transfer to a back-contacted conductive substrate.

It has been reported that films composed of perpendicularly oriented crystallites showed higher photoelectrochemical performance than that of films with nanocrystalline particles. For WO₃, there have been few works focusing on the photoelectrochemical behavior of perpendicularly oriented crystalline films. Herein, for the first time, WO₃ films consisting of perpendicularly oriented crystalline flakes were successfully fabricated by a wet process using anisotropic crystal growth of WO₃•H₂O with a layered crystal structure. Since the crystalline flakes were oriented normal to the substrate like a wall, we named this film a flake-wall film. Figure 1a shows the crystal structure of WO₃•H₂O. The octahedral WO₆(H₂O) units in which a tungsten atom is surrounded by a water molecule and five oxygen atoms are horizontally connected at four corners to form a layer and the layers are stacked through hydrogen bondings. The (010) crystal plane-selective growth parallel to the layer would result in production of crystalline flakes, as has been observed as flake-like morphology of WO₃•H₂O. Figure 1b shows a scanning electron microscope (SEM) image of particles prepared by solvothermal reaction of tungsten(VI) chloride (WCl₆) in ethanol at 373 K. Each particle is an assembly of a number of crystalline WO₃•H₂O flakes. If heterogeneous nucleation occurs only on a conductive substrate, self-organized crystal growth normal to the substrate is expected, since growth in other directions is terminated by collision with other flakes. In this study, a base layer of a nanocrystalline thin film was used for the enhancement of heterogeneous nucleation for the growth of perpendicularly oriented WO₃•H₂O crystallites, which were then transformed to monoclinic WO₃ crystallites by calcination.

Fig. 1. (a) Crystal structure of WO₃•H₂O. (b) SEM image of particles prepared by solvothermal reaction of WCl₆.

Tin-oxide (SnO₂)-coated glass was used for a transparent conductive substrate in this study. This substrate was precoated by nanocrystalline WO₃ thin films using a sol-gel technique according to the procedure by Augustynski and co-workers. The deposition of WO₃•H₂O was performed using a newly developed solvothermal method. A solution of 2 mmol WCl₆ in 70 mL ethanol was prepared in a glove box filled with dry air to avoid hydrolysis of WCl₆ by atmospheric humidity. The substrate coated with a nanocrystalline WO₃ thin film (5.25 cm²) was soaked in the ethanol solution of WCl₆ and heated in a 100-ml Teflon-lined autoclave at 373 K for 20 h. No appreciable deposition was observed on the conductive glass in the absence of the base WO₃ nanocrystalline layer. After cooling to room temperature, the
substrate was washed with water and dried at 393 K. The actual monomer for the nucleation and growth might be tungsten(VI) ethoxide produced by alcoholysis of WCl₆ upon dissolution in ethanol. The film prepared by the solvothermal reaction was calcined at 773 K for 2 h in air.

Fig. 2 XRD patterns of (a) SnO₂ glass, (b) nanocrystalline WO₃ thin film, (c) film-A, and (d) film-B (X: SnO₂, Y: WO₃•H₂O, and Z: monoclinic WO₃). Crystal structures of WO₃•H₂O and monoclinic WO₃ are also shown.

Figure 2 shows X-ray diffraction (XRD) patterns of the substrate and the prepared films. The XRD pattern of nanocrystalline WO₃ thin film shows the presence of monoclinic WO₃ indicated by the three characteristic diffractions at 2θ = 23–25°. The film prepared by solvothermal reaction (film-A) exhibited XRD patterns assigned to crystalline WO₃•H₂O (JCPDS card no. 43-0679) as well as to monoclinic WO₃ corresponding to the nanocrystalline base layer. It was found that the peak intensity of WO₃•H₂O 200 diffraction was relatively large compared with the XRD pattern of isotropic WO₃•H₂O powders, suggesting that most of the WO₃•H₂O (200) planes are parallel to the substrate. Post-calcination caused disappearance of the peaks assigned to WO₃•H₂O and enhancement of peaks assigned to monoclinic WO₃. In the pattern of the calcined film (film-B), a peak attributable to WO₃ 220 diffraction exhibited high intensity, suggesting selective orientation of the (220) planes parallel to the substrate. Crystal transformation to monoclinic WO₃ is considered to proceed through dehydration of hydroxyl groups in crystalline WO₃•H₂O.¹⁹,²⁰

Figure 3 shows top-view images of the prepared films observed by SEM. Flake-like morphology normal to the substrate was observed for both film-A and film-B. Thus, the calcination did not change the morphology, though the average thickness of flakes was slightly reduced from ca. 95 nm to ca. 80 nm by crystal transformation inducing shrinkage of interlayer distance. An SEM cross-sectional image of film-B shows that the crystalline flakes with height of ca. 3 μm were vertically deposited on the nanocrystalline WO₃ thin film (ca. 0.8-μm thickness) coated on SnO₂ glass. It is concluded that WO₃ flake-wall films were successfully fabricated on a transparent conductive substrate using a base layer.

The photoelectrochemical property of the prepared films for water oxidation was investigated using a three-electrode system: a platinum wire as a counter electrode and a silver/silver chloride (Ag/AgCl) electrode as a reference (+0.209 V vs. SHE) were used. Hereafter, the electrode potential is reported relative to the Ag/AgCl electrode. Figure 4 shows potential-current curves under chopped visible light irradiation (> 400 nm) from the back-side through the transparent substrate. The photocurrent of the nanocrystalline WO₃ thin film used for preparation of the flake-wall film was relatively small and saturated at relatively low anodic potential (ca. 0.4 V), suggesting poor photoabsorption ability of the base film. Film-A exhibited a dark anodic current at around 0.15–0.45 V. The current is attributable to redox reactions of WO₃•H₂O itself. The even smaller photocurrent for film-A than that of the base film indicates that WO₃•H₂O was photoinactive and the solvothermal reaction diminished the photoelectrochemical activity of the base film. On the other hand, significantly enhanced photocurrent of film-B suggests that crystallization to monoclinic WO₃ enhances the photoresponse of the flake-wall film for water oxidation.

Fig. 3 SEM top-view images of (a) nanocrystalline WO₃ thin film, (b) film-A, and (c) film-B. SEM cross-sectional image of (d) film-B (X: flakes, Y: nanocrystalline WO₃, and Z: SnO₂ glass).

Fig. 4 Current-potential plots for (a) nanocrystalline WO₃ thin film, (b) film-A, and (c) film-B illuminated with chopped visible light in an aqueous solution of 0.1 mol L⁻¹ sodium sulfate (Na₂SO₄). Right-side image shows an overview of the redox potentials with respect to the band potentials of WO₃ at pH 7 (CB: conduction band, VB: valence band, and Eₘₚ: flat band potential).
The photocurrent onset potential for film-B was observed at ca. +0.1 V. On the other hand, when 10vol% methanol was added to the electrolyte, the onset potential shifted to cathodic potential by ca. 0.2 V (see Fig. S1 in ESI), which is close to the previously reported potentials for a WO₃ electrode. This negative shift of the onset potential suggests that direct hole transfer to methanol to form CH₂OH radical is more efficient than to water to form hydroxyl radical. Since the CH₂OH radical exhibited the large negative redox potential, which can transfer an electron to the conduction band of WO₃, the possibility of back-electron transfer is expected to be negligible. As previously reported, the photocurrent was increased by ca. two times by the addition of methanol owing to the simple current doubling effect and/or the higher reactivity of methanol than that of water.

Photocurrent density as a function of light intensity and (B) action spectra of IPCEs for film-B (circles) and film-C (triangles) in an aqueous Na₂SO₄ solution. The photocurrent was measured at +1.2 V vs Ag/AgCl. Diffuse transmittance spectrum of film-B is also shown. Action spectra of IPCEs for film-B (circles) and film-C (triangles) in an aqueous Na₂SO₄ solution. The photocurrent was measured at +1.2 V vs Ag/AgCl. Diffuse transmittance spectrum of film-B is also shown.

Notes and references